Vapor-Liquid Equilibria for Systems of 1-Butanol with 2-Methyl-1-butanol, 3-Methyl-1-butanol, 2-Methyl-2-butanol, and 3-Methyl-2-butanol at 30 and 100 kPa

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Vapor-liquid equilibrium data were measured for binary systems of 1-butanol with 2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-2-butanol, and 3-methyl-2-butanol at 30 and 100 kPa. The experimental data obtained in this work are thermodynamically consistent according to a point-to-point consistency test, and deviation from ideal behavior is small in all cases. They can be equally well correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations.

Introduction

The most common operation in the chemical industry is the separation of liquid mixtures through distillation. Efficient design of distillation equipment requires quantitative knowledge of vapor-liquid equilibria (VLE) in binary or multicomponent mixtures.

VLE data of the system under consideration can be obtained experimentally or by using prediction models such as group contribution methods. In process engineering applications, especially in phase-equilibria calculations, the best-known and most widely used of the group contribution methods is the UNIFAC method, in its original (1) or modified (2) form. The generation of reliable interaction parameters of the functional groups needs a lot of experimental information.

The data reported here are not available in the literature. The first aim of this work is to provide consistent data of binary systems, in which both components are alcohols (primary, secondary, or tertiary), and to improve the VLE data bank.

Experimental Section

Chemicals. All components used in this study were purchased from Aldrich Chemical Co.: 1-butanol (27,067-9; 99%), 2-methyl-1-butanol (13,305-1; 99+%), 3-methyl-1-butanol (30,943-5; 99+%), 2-methyl-2-butanol (15,246-3; 99%), and 3-methyl-2-butanol (11,094-9; 98%). The purities of all chemicals were checked by gas chromatography (GC), and the chemicals were used without further purification. The water content was small in all chemicals (<0.05%). The physical properties of these components are listed in Table 1 together with literature values (3, 4).

Apparatus and Procedure. The apparatus used in this work was an all-glass, dynamic recirculating still described by Walas (5), equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik (Germany) is capable of handling pressures *P* from 0.25 to 400 kPa, and temperatures *T* up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact and also in contact with the temperature-sensing element. The equilibrium temperature was measured with a digital Fisher thermometer with an accuracy of 0.1 K, and the pressure with a digital manometer with an accuracy of 0.01 kPa. VLE data were obtained at two pressures (30 and 100 kPa) for all systems.

Table 1. Densities *d*, Refractive Indexes *n*, and Boiling Points *T*$_b$ of the Chemicals Used in This Study

compound	d(293.15 K)/ (g cm^{-3})		n(D, 293.15 K)		T_b(100.0 kPa)/ K	
	exptl	lit. (3)	exptl	lit. (3)	exptl	lit.^{a}
1-butanol	0.809 50	0.8098	1.3988	1.3993	390.15	390.49
2-methyl-1-butanol	0.817 99	0.8152	1.4100	1.4092	401.55	401.48
3-methyl-1-butanol	0.808 36	0.8092	1.4061	1.4053	404.45	403.97
2-methyl-2-butanol	0.809 00	0.8059	1.4046	1.4052	374.85	374.73
3-methyl-2-butanol	0.817 87	0.8180	1.4090	1.4089	383.55	na

^{a} Calculated using the Antoine coefficients from ref 4.

Table 2. Vapor Pressures *P*$_i$°, Antoine Coefficients *A*, *B*, and *C*, and Mean Average Deviations MAD(*P*$_i$°) of the Pure Components

component	temp range/K	Antoine coefficients^a			MAD-(*P*$_i$°)^b
		A	B	C	
1-butanol	315-390	15.3763	3253.99	-88.124	0.08
2-methyl-1-butanol	330-405	14.8958	3107.20	-99.883	0.11
3-methyl-1-butanol	340-405	14.9010	3141.77	-99.193	0.13
2-methyl-2-butanol	308-375	14.5382	2739.80	-98.888	0.22
3-methyl-2-butanol	325-385	14.4293	2754.37	-103.139	0.14

^{a} ln (P_i°/kPa) = $A - B/((T/K) + C)$. ^{b} MAD(P_i°) = $\Sigma |P°_{exptl} - P°_{calcd}|/N$ (N = number of data points).

In each experiment, the work pressure was fixed and the heating and shaking system of the liquid mixture was connected. This was kept at the boiling point for 15 min to ensure the stationary state. Once it was certain that the stationary state was reached, samples of the liquid and vapor of the Cottrell pump were taken. The extractions were carried out with special syringes which allowed us to take small-volume samples in a system under partial vacuum.

Samples of 3 μL were withdrawn from the condensed vapor and liquid streams of the still and were analyzed with a Hewlett-Packard 5890 S-II gas chromatograph (GC) with a flame ionization detector. The GC response peaks were integrated by using a Hewlett-Packard 3396 integrator. The GC column used was a fused silica capillary column, SUPELCOWAX 10, of 60-m length and 0.2-mm internal diameter.

The GC was calibrated with gravimetrically prepared standard solutions. A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. However, with repeated measurements, the standard devi-

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Table 3. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the 1-Butanol (1) + 2-Methyl-1-butanol (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
30.00	0.000	0.000	370.15		
	0.055	0.082	369.45	1.019	0.999
	0.114	0.175	368.65	1.043	0.997
	0.179	0.254	367.85	1.045	0.997
	0.236	0.334	367.05	1.035	0.999
	0.286	0.399	366.45	1.024	1.003
	0.351	0.461	365.85	1.011	1.009
	0.438	0.556	364.95	1.002	1.015
	0.518	0.629	364.05	1.002	1.014
	0.593	0.688	363.35	1.007	1.007
	0.650	0.752	362.75	1.012	0.999
	0.729	0.811	362.05	1.017	0.989
	0.797	0.863	361.35	1.017	0.911
	0.858	0.905	360.85	1.012	1.012
	0.899	0.936	360.45	1.008	1.045
	0.941	0.964	360.05	1.004	1.102
	0.969	0.982	359.85	1.001	1.159
	1.000	1.000	359.65		
100.00	0.000	0.000	401.55		
	0.054	0.089	400.65	1.118	1.002
	0.125	0.179	399.70	1.061	1.007
	0.167	0.241	399.10	1.041	1.010
	0.227	0.317	398.20	1.024	1.014
	0.288	0.382	397.45	1.018	1.016
	0.340	0.434	396.85	1.018	1.016
	0.411	0.521	395.95	1.021	1.014
	0.507	0.612	394.80	1.027	1.009
	0.593	0.691	393.80	1.030	1.006
	0.667	0.755	392.90	1.028	1.010
	0.761	0.821	391.95	1.020	1.028
	0.825	0.878	391.35	1.013	1.056
	0.891	0.926	390.95	1.006	1.103
	0.959	0.975	390.35	1.001	1.177
	1.000	1.000	390.15		

Table 4. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the 1-Butanol (1) + 3-Methyl-1-butanol (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
30.00	0.000	0.000	372.25		
	0.033	0.055	371.65	1.013	1.008
	0.060	0.100	371.35	1.025	1.001
	0.099	0.160	370.65	1.023	1.004
	0.149	0.234	369.95	1.023	0.999
	0.176	0.276	369.55	1.038	0.992
	0.227	0.343	368.85	1.029	0.989
	0.279	0.402	368.15	1.010	0.994
	0.321	0.451	367.65	1.006	0.991
	0.395	0.533	366.55	1.012	0.993
	0.468	0.600	365.65	0.998	1.006
	0.545	0.675	364.65	1.006	0.999
	0.628	0.750	363.65	1.013	0.983
	0.703	0.805	362.85	1.005	0.996
	0.774	0.861	362.05	1.011	0.967
	0.852	0.912	361.25	1.007	0.970
	0.907	0.946	360.75	1.003	0.969
	0.951	0.974	360.35	1.002	0.902
	1.000	1.000	359.65		
100.00	0.000	0.000	404.45		
	0.037	0.058	403.55	0.995	1.005
	0.098	0.149	402.45	1.000	1.006
	0.147	0.217	401.65	0.997	1.006
	0.173	0.254	401.15	1.008	1.006
	0.217	0.310	400.55	1.001	1.003
	0.255	0.360	399.95	1.009	0.998
	0.304	0.419	399.25	1.008	0.994
	0.369	0.489	398.25	1.003	0.999
	0.467	0.583	396.75	0.994	1.017
	0.534	0.649	395.75	1.002	1.015
	0.621	0.729	394.45	1.012	1.010
	0.690	0.784	393.75	1.004	1.009
	0.770	0.848	392.75	1.007	0.992
	0.849	0.903	391.75	1.008	1.001
	0.905	0.941	391.15	1.006	0.989
	0.948	0.969	390.75	1.003	0.963
	1.000	1.000	390.15		

ation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made of each liquid and each vapor composition.

Table 5. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the 2-Methyl-2-butanol (1) + 1-Butanol (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
30.00	0.000	0.000	359.85		
	0.024	0.041	359.60	0.919	0.993
	0.055	0.094	359.00	0.930	0.996
	0.099	0.161	358.30	0.919	0.997
	0.125	0.206	357.80	0.943	0.995
	0.170	0.265	357.05	0.923	1.003
	0.228	0.350	356.05	0.946	0.998
	0.289	0.434	354.85	0.976	0.996
	0.366	0.536	353.55	1.003	0.973
	0.437	0.614	352.45	1.010	0.958
	0.529	0.702	351.15	1.007	0.941
	0.621	0.781	349.70	1.016	0.919
	0.705	0.840	348.65	1.007	0.910
	0.772	0.880	347.65	1.007	0.930
	0.834	0.917	346.85	1.007	0.913
	0.889	0.945	346.20	1.002	0.935
	0.947	0.973	345.40	1.004	0.999
	1.000	1.000	344.95		
100.00	0.000	0.000	390.15		
	0.021	0.034	390.05	0.929	0.994
	0.048	0.074	389.65	0.933	0.993
	0.092	0.144	388.70	0.976	0.995
	0.124	0.186	388.15	0.946	1.001
	0.153	0.223	387.75	0.931	1.003
	0.221	0.325	386.35	0.982	0.997
	0.271	0.383	385.50	0.971	1.005
	0.361	0.491	383.95	0.985	1.001
	0.351	0.490	384.05	1.007	0.985
	0.435	0.573	382.85	0.990	0.991
	0.511	0.652	381.75	0.998	0.969
	0.613	0.741	380.15	0.998	0.969
	0.678	0.795	379.30	0.996	0.955
	0.757	0.850	378.05	0.997	0.972
	0.823	0.895	377.15	0.997	0.964
	0.881	0.930	376.40	0.994	0.986
	0.946	0.968	375.35	1.001	1.025
	1.000	1.000	374.85		

Results and Discussion

The experimental vapor pressure data of pure components, P_i°, were measured with the same recirculating still. Table 2 summarizes the fit of the experimental vapor pressures to the Antoine equation, in the range of work temperatures, together with the mean absolute deviation between experimental and calculated vapor pressures, MAD(P_i°).

The VLE data for all binary systems have been obtained at 30 and 100 kPa and are presented in Tables 3–6. The T–x–y diagram for the 2-methyl-2-butanol + 1-butanol system is shown in Figure 1, as an illustration.

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = y_i P / x_i P_i^\circ \tag{1}$$

The Poynting factor was considered as unity at the experimental conditions of this work (4), and the vapor pressures P_i° were calculated with the Antoine equation (Table 2). The fugacity coefficient calculated on the basis of the Redlich–Kwong equation of state (6), with the modification introduced by Soave (7), is nearly unity. The γ_i values are listed in Tables 3–6.

The VLE data were first tested for thermodynamic consistency using the point-to-point method of Van Ness et al. (8), modified by Fredenslund et al. (1). A four-parameter Legendre polynomial was used for the excess Gibbs free energy. The measured binary data were considered to be thermodynamically consistent when the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, MAD(y), was less than

Table 6. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the 3-Methyl-2-butanol (1) + 1-butanol (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
30.00	0.000	0.000	359.85		
	0.025	0.032	359.65	0.950	1.002
	0.061	0.079	359.35	0.975	1.003
	0.107	0.136	358.95	0.984	1.006
	0.136	0.170	358.75	0.971	1.009
	0.185	0.231	358.35	0.985	1.009
	0.238	0.290	357.95	0.980	1.014
	0.298	0.359	357.55	0.986	1.011
	0.356	0.424	357.05	0.995	1.013
	0.431	0.509	356.45	1.011	1.005
	0.505	0.580	355.95	1.006	1.010
	0.573	0.645	355.45	1.007	1.012
	0.639	0.707	354.95	1.011	1.011
	0.716	0.775	354.35	1.016	1.015
	0.774	0.826	353.95	1.020	1.002
	0.833	0.874	353.55	1.019	1.007
	0.894	0.921	353.15	1.019	1.012
	0.947	0.961	352.85	1.016	1.032
	1.000	1.000	352.55		
100.00	0.000	0.000	390.15		
	0.026	0.031	389.95	0.956	1.005
	0.061	0.074	389.75	0.986	1.003
	0.107	0.128	389.35	0.979	1.008
	0.139	0.166	389.05	0.985	1.011
	0.185	0.219	388.75	0.988	1.011
	0.237	0.277	388.45	0.986	1.010
	0.298	0.343	387.95	0.988	1.016
	0.355	0.402	387.55	0.986	1.020
	0.430	0.485	386.95	1.001	1.017
	0.501	0.552	386.55	0.992	1.025
	0.575	0.625	386.05	0.996	1.025
	0.642	0.689	385.65	0.996	1.025
	0.714	0.757	385.15	1.001	1.022
	0.772	0.808	384.80	1.000	1.025
	0.835	0.862	384.45	0.999	1.031
	0.892	0.911	384.15	0.998	1.037
	0.944	0.954	383.85	0.998	1.042
	1.000	1.000	383.55		

0.01. The results of this test for the binary systems under consideration are shown in Table 7.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (9). For fitting the binary parameters, the Rosenbrok method (10) was used to minimize the following objective function, using the activity coefficients obtained from the consistency test as experimental values:

$$F = \sum \left(\frac{\gamma_{exptl} - \gamma_{calcd}}{\gamma_{exptl}} \right)^2 \qquad (2)$$

The correlation was very good with all equations, and the mean absolute deviations between experimental and calculated temperatures, MAD(T), and vapor compositions, MAD-(y), were on the order of the estimated experimental uncertainties.

Finally, the VLE data for these mixtures have been predicted by using the original and modified UNIFAC methods. The activity coefficients for each component in the mixtures are estimated by using the group interaction, volume, and area parameters reported by Danner and Daubert (11) for the original UNIFAC method (1), and by Gmehling et al. for the modified UNIFAC method (2). The mean absolute deviations between experimental and predicted vapor phase compositions and temperatures are presented in Table 8.

It can be observed that the descriptions of those systems containing primary and secondary alcohols by the modified (2) and original (1) UNIFAC methods are comparable and very good at both pressures. However, in the 2-methyl-2-
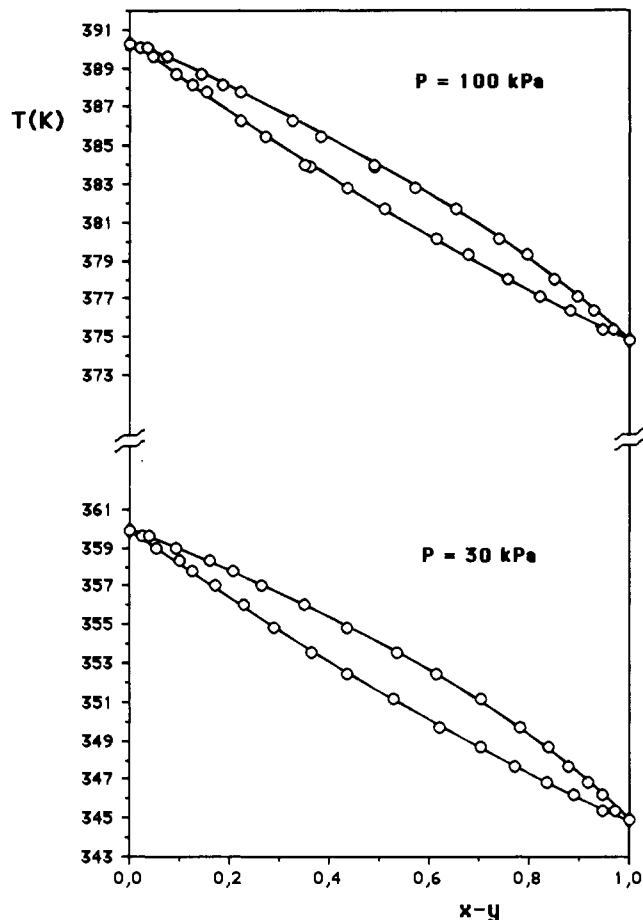

Figure 1. Vapor–liquid equilibrium temperature T of the system 2-methyl-2-butanol (1) + 1-butanol (2) at $P = 30$ and 100 kPa as a function of the mole fraction of component 1.

Table 7. Results of the Thermodynamic Consistency Test for the Systems Used in This Study at 30 and 100 kPa

	MAD(y)[a]	
system	$P = 30$ kPa	$P = 100$ kPa
1-butanol + 2-methyl-1-butanol	0.0044	0.0046
1-butanol + 3-methyl-1-butanol	0.0050	0.0039
2-methyl-2-butanol + 1-butanol	0.0063	0.0053
3-methyl-2-butanol + 1-butanol	0.0057	0.0046

[a] MAD(y) = $\sum |y_{exptl} - y_{calcd}|/N$ (N = number of data points).

Table 8. Mean Average Deviations between Experimental and Predicted VLE Data for the Systems Used in This Study Using the Original (1) and Modified (2) UNIFAC Methods

		MAD(y)		MAD(T)	
system	P/ kPa	original UNIFAC	modified UNIFAC	original UNIFAC	modified UNIFAC
1-butanol + 2-methyl-1-butanol	30	0.0042	0.0043	0.20	0.19
	100	0.0055	0.0056	0.47	0.48
1-butanol + 3-methyl-1-butanol	30	0.0034	0.0036	0.07	0.11
	100	0.0017	0.0016	0.07	0.12
2-methyl-2-butanol + 1-butanol	30	0.0096	0.0216	0.25	0.94
	100	0.0046	0.0172	0.26	1.12
3-methyl-2-butanol + 1-butanol	30	0.0028	0.0041	0.17	0.12
	100	0.0044	0.0048	0.10	0.03

butanol + 1-butanol system the mean absolute deviations are not as good, even worse, using the modified rather than original UNIFAC method.

Even though the experimental data set presented in this work is small, the results in Table 8 seem to corroborate the idea of Gmehling et al. (2) that "the use of different main groups for the primary, secondary, and tertiary alcohols would be very helpful for describing their different behavior. This

would however involve a great increase in the number of required group interaction parameters, and the present limited data base does not allow a fit of the required parameters for three alcohol main groups with all the other main groups".

The majority of the VLE data for systems containing alcohols available in the literature are formed by an alcohol and another component. The differences between experimental and calculated data mentioned before could be justified by the fact that the systems included here are formed by two alcohols (primary–primary, primary–secondary, and primary–tertiary). Furthermore, these data can contribute to the best knowledge of OH-group behavior.

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